Statistical Mechanics and Thermodynamics of Simple Systems

Handout 10

Heat capacity of a gas of heteronuclear diatomic molecules

We restrict ourselves to heteronuclear diatomic molecules (i.e. both atoms that make up the molecule are different, e.g. CO, HD). Homonuclear diatomic molecules (e.g. H_2, N_2, O_2) have additional quantum mechanical constraints imposed on them by exchange symmetry.

We assume that the translational, rotational and vibrational motions are independent, which is valid providing the characteristic energy scales of each degree of freedom are distinct. With this assumption, one can write

$$Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}, \tag{1}$$

and hence $U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}}$. Consider each degree of freedom in turn:

- From the equipartition theorem, $U_{\text{trans}} = \frac{3}{2}RT$ per mole, so $C_V^{\text{trans}} = \frac{3}{2}R$.

- Treat the vib. part as N SHOs. This means that eqn (**??**) applies but with N instead of $3N$ in the prefactor. When $T \gg \Theta_E$, $C_V^{\text{vib}} \to R$ per mole.

- Treat the rot. motion as a rigid rotor. The energy levels are quantized:

$$E_l = \frac{\hbar^2}{2I}l(l+1), \qquad (I = \mu R^2), \tag{2}$$

  where l is an integer ($l \geq 0$), I is the moment of inertia of the molecule, $\mu = m_1 m_2/(m_1 + m_2)$ is its reduced mass, and R is the separation of the atoms. Each energy level is $(2l+1)$-fold degenerate, so that the single-molecule partition function is

$$\begin{aligned} Z_{\text{rot}}(1) &= \sum_{l=0}^{\infty}(2l+1)\,e^{-\beta\frac{\hbar^2}{2I}l(l+1)} \\ &= 1 + 3e^{-2\frac{\Theta_{\text{rot}}}{T}} + 5e^{-6\frac{\Theta_{\text{rot}}}{T}} + \ldots, \end{aligned} \tag{3}$$

  where $\Theta_{\text{rot}} = \hbar^2/(2Ik_B)$. When $T \gg \Theta_{\text{rot}}$,

$$Z_{\text{rot}}(1) \approx \int_0^{\infty}(2l+1)\,e^{-\frac{\Theta_{\text{rot}}}{T}l(l+1)}\,dl = \frac{T}{\Theta_{\text{rot}}}, \tag{4}$$

  Hence, $C_V^{\text{rot}} \to R$ per mole.
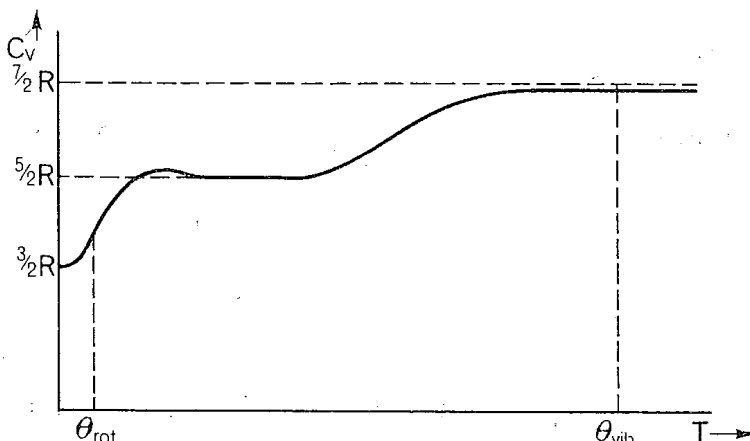
The molar heat capacity C_V of an ideal gas of heteronuclear diatomic molecules, showing the stepwise increases in heat capacity as, first, the rotational modes, and second, the vibrational modes become thermally activated.

Models of the Earth's atmosphere

Isothermal atmosphere: Assume the atmosphere is an ideal gas at constant temperature T. Gravitational potential energy increases with height above the Earth's surface, so the probability of a molecule reaching height h is given by the Boltzmann probability,

$$P(h) \propto \exp(-\frac{mgh}{k_{\mathrm{B}}T}), \tag{5}$$

where m is the mass of an air molecule. At fixed T, $P(h)$ is proportional to the number density of molecules, which is in turn proportional to pressure ($p = nk_{\mathrm{B}}T$). Hence,

$$\frac{p(h)}{p(0)} = \exp(-\frac{Mgh}{RT}), \tag{6}$$

where $M \simeq 0.029 \, \mathrm{kg \, mol^{-1}}$ is the molar mass of air (mostly nitrogen) and $g = 9.81 \, \mathrm{m \, s^{-2}}$.

Adiabatic atmosphere: This is a slightly better approximation to the Earth's atmosphere. Consider a parcel of air which undergoes adiabatic expansion as it rises. For an adiabatic expansion of an ideal gas, $pV^{\gamma} = \mathrm{constant}$, where $\gamma = C_p/C_V$, and $pV = RT$ for 1 mole, so

$$\frac{\mathrm{d}p}{p} = -\frac{\gamma}{\gamma - 1}\frac{\mathrm{d}T}{T}. \tag{7}$$

From (6),

$$\frac{\mathrm{d}p}{p} = -\frac{Mg}{RT}\mathrm{d}h. \tag{8}$$

Equating (7) and (8) and integrating, we obtain

$$T(h) = T(0) - Lh, \tag{9}$$

where $L = Mg/C_p$ is known as the *adiabatic lapse rate*. For dry air, $L = 9.7 \times 10^{-3} \, \mathrm{K \, m^{-1}}$, assuming $C_p = 7R/2$. In reality, $L \simeq 6.5 \times 10^{-3} \, \mathrm{K \, m^{-1}}$. To obtain the variation of pressure with height, substitute (9) in (8) and integrate to give

$$\frac{p(h)}{p(0)} = \left[1 - \frac{Lh}{T(0)}\right]^{\frac{Mg}{RL}}. \tag{10}$$

The figure shows the atmospheric pressure as a function of height above the Earth's surface for the isothermal and adiabatic atmospheric models.